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(54) LIQUID DETERGENT COMPOSITIONS

(71) We, THE PROCTER & GAMBLE COMPANY, a Corporation organised under the laws of the State of Ohio, United States of America, of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

This invention relates to concentrated heavy duty liquid compositions for use in cool water fabric laundering. More particularly, it relates to a clear stable liquid detergent composition containing a nonionic surfactant component and an alkaline earth metal salt of an anionic surfactant component having the ability to remove soils from fabrics and which also provide adequate suds during the wash and easy rinsing after the wash.

In formulating a liquid detergent composition for consumer use it is important to provide a formulation whose performance characteristics are similar to the more widely available granular products. Thus the cleaning performance formulations for that reason. Nonionics are also known as low foamers whose foam is persistent at low concentrations even though they do not foam freely at higher concentrations. Under these conditions, the housewife will tend to overuse product to get the desired washing suds level and then have to contend with a persistent foam during the rinsing operation. Use of nonionics which do give easy rinsing characteristics generally do not form clear stable liquid compositions nor do they clean as well as higher sudsing nonionics. These problems may be particularly important when washing and rinsing at ambient temperatures which is the normal practice in some countries, which is desirable for modern fabrics, and which has been suggested as an energy conservation measure.

Heavy duty liquid compositions providing good detergency performance and exhibiting good wash suds and easy rinsing in cool water are described in copending application No. 11922/75 (Serial No. 1491603). The compositions include primary alcohol ethoxylates having a chain length of 7 to 12 carbon atoms and condensed with from 2 to 15 moles of ethylene oxide per mole of alcohol, an alkanolamine salt of certain anionic surfactants and an excess of alkanolamine.

By the present invention it has been discovered that using the anionic surfactant as its magnesium or calcium salt rather than as the alkanolamine salt thereof and omitting the excess alkanolamine, the range of the suitable nonionic surfactant component can be extended to include species that heretofore were unsuitable. Compositions containing the heretofore unsuitable species tended to form gels rather than liquid compositions and in use the suds during the wash was too low in cool water washing. Further, such relatively insoluble nonionics used alone or in combination with sodium or other monovalent salts of anionic surfactants generally did not clean as well at ambient temperatures. By this invention it has been discovered that the alkaline earth metal, especially magnesium and calcium, salts of anionic surfactants are superior to the alkanolamine salts of anionic surfactants in solubilizing the nonionic surfactant into the composition without causing gelling. This improved solubilization of the nonionic surfactant in compositions containing alkaline earth metal anionic surfactants provides for better cleaning and improved suds in the wash and easy rinsing in cool water laundering. Another benefit of the discovery that the alkaline earth metal salts of anionic surfactants are better solubilizers than the alkanolamine salts of anionic surfactants is that there is no need to use electrolyte salts to prevent gelling in liquid compositions which has heretofore been the practice.

The use of magnesium and/or calcium ions in detergent compositions to provide increased detergency benefits has been disclosed heretofore.

U.S. Patent 2,908,651, entitled LIQUID DETERGENT COMPOSITION, October 13, 1959, discloses single-phase, clear, concentrated liquid detergents containing, inter alia, alkanolamines, magnesium or calcium salts, alcohols, and alkyl aryl sulfonates. This patent describes in some detail the problems associated with the preparation of single-phase, clear liquid detergents.

U.S. Patent 2,691,636, entitled DETERGENT COMPOSITIONS, October 12, 1954, relates to synthetic detergent compositions and their use, inter alia, in their calcium and magnesium form.

U.S. Patent 2,766,212, entitled DETERGENTS, October 9, 1956, discloses and claims, inter alia, the use of polyvalent metals such as the chlorides, sulfates, acetates, etc., of magnesium, calcium, etc., in combination with anionic detergents which are sulfated ethoxylated alcohols.

U.S. Patent 3,202,613, entitled PROCESS FOR PRODUCTION OF DETERGENT COMPOSITIONS, August 24, 1965, teaches the use of magnesium sulfate in low bulk density built detergents.

U.S. Patent 3,440,171, entitled SURFACE ACTIVE COMPOSITIONS, April 22, 1969, teaches the use of various salts, including magnesium salts, as degellants for fluid mixtures of alkyl benzene sulfonic acids and alkanolamines.

U.S. Patent 3,282,852, entitled HEAVY DUTY LIQUID DETERGENTS, November 1, 1966, teaches, inter alia, hydrotropes, nonionics and higher alkaryl sulfonates in their alkanolamine or magnesium salt form.

U.S. Reissue Patent Re. 27,096, reissued March 23, 1971, teaches a high sudsing detergent composition comprising a synergistic mixture of olefin sulfonates, alkyl benzene sulfonates and alkyl ether sulfates and teaches that magnesium salts of these materials may be employed.

U.S. Patent 3,718,609, entitled LIQUID DETERGENT COMPOSITIONS, February 27, 1973, relates to dual layer liquid detergents which can contain magnesium surfactants.

U.S. Patent 3,686,098, entitled NOVEL DETERGENT COMPOSITION, August 22, 1972, relates to di-anionic detergents and the water-soluble calcium, magnesium, etc., salts thereof.

As can be seen from the foregoing, polyvalent metal ions such as calcium and magnesium have been employed in a variety of detergent compositions. Additional references in this regard include the following:

U.S. Patents 3,819,539, June 25, 1974; 3,700,607, October 24, 1972; 3,697,587, October 10, 1972; 3,679,611, July 25, 1972; 3,679,609, July 25, 1972; 3,634,269, January 11, 1972; 3,577,347, May 4, 1971 (relating to stable, non-gritty cleanser composition comprising detergent mixture which can be an alkyl benzene sulfonate and a nonionic surfactant, certain magnesium salts, and a chlorine bleach); 3,505,395, April 7, 1970; 3,384,595, May 21, 1968; 3,345,300, October 3, 1967; 3,325,412, June 13, 1967; 3,303,137, February 7, 1967; 3,274,117, September 20, 1966; 3,265,624, August 9, 1966 (chlorine bleach-containing composition); 3,256,202, June 14, 1966; 3,053,771, September 11, 1962; 3,072,580, January 8, 1963; 2,857,370, October 21, 1958; 2,731,442, January 17, 1956; 2,166,314, July 18, 1939; 2,562,155, July 24, 1951; 2,037,566, April 14, 1936; 2,658,072, November 3, 1953; and 2,717,243, September 6, 1955.

In addition to the foregoing, U.S. Patents 3,869,399, issued March 4, 1975, 3,594,323, issued July 20, 1971, and the references cited therein, disclose various heavy duty liquid detergents.

It is the object of this invention to provide heavy duty clear stable liquid detergent compositions comprising a significant amount of an alkaline earth metal salt of an anionic surfactant which exhibits adequate sudsing during the wash and good rinsing after the wash under cool water washing conditions.

This and other objects are obtained herein as will be seen from the following disclosure.

The present invention encompasses clear, stable single phase heavy-duty liquid detergent compositions, comprising:

(a) from 10% to 50% by weight of the composition based on the free acid form of an anionic detersive surfactant which is either a sulfate or sulfonate, or mixtures thereof;

(b) sufficient magnesium ion or calcium ion, or mixtures thereof, to neutralize at least 75% of the free acid form of said anionic detergent;

(c) from 5% to 50% by weight of a non-ionic surfactant produced by the condensation of from 2 to 15 moles of ethylene oxide with one mole of a primary or secondary alcohol having a straight or branched alkyl chain containing 8 to 18 carbon atoms, said nonionic surfactant being further characterized by having an HLB of from 8 to 18;

(d) from 0% to 10% of an alkanolamine wherein the alkanol moiety contains from 2 to 4

carbon atoms preferably mixtures of mono- and triethanolamine; and

(e) the balance of the composition comprising mixtures of water and water-soluble solvents, there being at least enough water-soluble solvent to lower the viscosity to 300 centipoise said composition having at least 35% by weight of (a) plus (c) and being substantially free of agents which cause phase separation and/or gelling and, said composition preferably having a pH of less than about 8.6, more preferably from about 7.4 to about 8.4. . .

DETAILED DESCRIPTION OF THE INVENTION

The clear stable liquid detergent compositions of this invention contain an alkaline earth metal salt of an anionic surfactant and a nonionic surfactant as essential ingredients in a suitable solvent carrier. The description of these materials and optional materials follow.

The Anionic Surfactant

The anionic surfactant is a calcium or magnesium salt of an organic anionic surfactant. Most preferred salts are the magnesium salts. The anionic surfactant provides improved oil and grease removal when used in these compositions as compared with the corresponding alkali metal salts.

The anionic component of the instant detergent compositions is preferably an organic sulfuric reaction product having in its molecular structure an alkyl group containing from about 8 to about 22 carbon atoms and a sulfonic acid or sulfuric acid ester group, or mixtures thereof. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants which can be used in the present invention are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8–C_{18}) carbon atoms produced from the glycerides of tallow or coconut oil; paraffin sulfonates, containing from about 10 to about 20 carbon atoms; and, preferably, alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 14 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099, and 2,477,383, incorporated herein by reference. Linear straight chain alkyl benzene sulfonates in which the average of the average of the alkyl groups is about 13 carbon atoms, abbreviated as C_{13}LAS, as well as mixed $C_{11.2\ (avg.)}$ LAS are typically used. C_{11}–C_{14} branched chain alkyl benzene sulfonates (ABS), which are excellent sudsers, can also be used.

Examples of commercially available alkyl benzene sulfonates (free acid form) useful in the instant invention include Conoco SA 515, SA 597, and SA 697, all marketed by the Continental Oil Company, and Calsoft LAS 99, marketed by the Pilot Chemical Company.

Other anionic surfactant compounds herein include the alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; coconut oil fatty acid monoglyceride sulfonates and sulfates; and alkyl phenol ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain about 8 to about 12 carbon atoms.

Other useful anionic surfactants herein include the esters of α-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the ester group; 2-acyloxy- alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; paraffin sulfonates having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms in the alkyl group; olefin sulfonates containing from about 12 to 24 carbon atoms in the alkyl group; and β-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Preferred water-soluble anionic organic surfactants herein include linear alkyl benzene sulfonates containing from about 10 to about 18 carbon atoms in the alkyl group; branched alkyl benzene sulfonates containing from about 10 to about 18 carbon atoms in the alkyl group; the tallow range alkyl sulfates; the coconut range alkyl glyceryl sulfonates; alkyl ether (ethoxylated) sulfates wherein the alkyl moiety contains from about 10 to 18 carbon atoms and wherein the average degree of ethoxylation varies between 1 and 12, especially 3 to 9; the sulfated condensation products of tallow alcohol with from about 3 to 12, especially 6 to 9, moles of ethylene oxide; and olefin sulfonates containing from about 14 to 16 carbon atoms; as hereinabove defined.

Specific preferred anionics for use herein include: the linear C_{10}–C_{14} alkyl benzene sulfonates (LAS); the branched C_{10} to C_{14} alkyl benzene sulfonates (ABS); the tallow alkyl sulfates; the coconut alkyl glyceryl ether sulfonates; the sulfated condensation products of mixed C_{10}–C_{18} tallow alcohols with from about 3 to about 14 moles of ethylene oxide; and the mixtures of higher fatty acids containing from 10 to 18 carbon atoms.

It is to be recognized that any of the foregoing anionic surfactants can be used separately herein or as mixtures. Moreover, commercial grades of the surfactants can contain non-

interfering components which are processing by-products. For example, commercial C_{10}–C_{14} alkaryl sulfonates can comprise alkyl benzene sulfonates, alkyl toluene sulfonates, alkyl naphthalene sulfonates and alkyl poly-benzenoid sulfonates. Such materials and mixtures thereof are fully contemplated for use herein.

The acid form of the anionic surfactant may be converted to the alkaline earth metal salt form either prior to admixture with the semi-polar nonionic detergent or thereafter. For example, a source of magnesium or calcium may be added to the detergent mixture under desirable reaction conditions to form the desired salts. Calcium and magnesium chloride, calcium and magnesium sulfate, calcium and magnesium acetate or calcium and magnesium hydroxide are examples of magnesium and calcium sources. In a preferred variation, the alkaline earth ion is added to provide electrical neutrality for the anionic surfactant.

Compositions of this invention contain from about 10% to about 50%, preferably from about 15% to about 45%, most preferably from about 20% to about 40%, by weight of the composition based on the acid form of the anionic surfactant.

The Nonionic Surfactant

The compositions of this invention contain as an essential ingredient about 5% to about 50%, preferably from about 10% to about 35%, and most preferably from about 10% to about 20%, by weight of a nonionic surfactant derived by the condensation of ethylene oxide with a primary or secondary alcohol. (Secondary alcohols are preferred for cleaning reasons). The general formula for the nonionic surfactant is $C_nH_{2n+1}O(CH_2–CH_2O)_eH$. It will be appreciated that the molecule consists of a lipophilic portion derived from the alcohol and a hydrophilic portion derived from the ethylene oxide. The number of moles of ethylene oxide condensed with one mole of alcohol and can be defined as ethoxylate number. The ethoxylate number may refer to the number of moles of ethylene oxide condensed in a single species, i.e., a pure compound, but for commercial materials it represents an average.

In the lipophilic portion of the molecule n is the number of carbons in the alkyl chain of the primary alcohol precursor and is defined as carbon number. For this invention the carbon chain of the alcohol may be straight or branched.

Examples of suitable primary straight chain alcohols are the linear primary alcohols obtained from the hydrogenation of vegetable or animal oil fatty acids such as coconut, palm kernel and tallow fatty acids, or by ethylene build-up reactions (Ziegler process) and subsequent hydrolysis of the terminal double bond. Preferred alcohols are n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tetradecyl, n-hexadecyl and n-octacecyl and mixtures thereof. Suitable commercially available ethoxylated alcohols are sold under the trademark "Alfonic" by Conoco Chemicals, Continental Oil Company, Saddlebrook, New Jersey.

Examples of suitable primary branched chain alcohols are those obtained from the well known Oxo process in which linear olefins are reacted with carbon monoxide and hydrogen to produce aldehydes which are then hydrogenated to give alcohols. Both linear and branched chain alcohols are formed. Commercially available ethoxylates made from these alcohol blends suitable for this invention are marketed by Royal Dutch Shell N.V. under the trademarks "Dobanol" and "Neodol".

Commercially available ethoxylates made from secondary alcohols which are suitable for this invention include Tergitol (Registered Trade Mark) 15-S-9 marketed by Union Carbide Corporation, Kyro EOB marketed by The Procter & Gamble Company and Softanol 120 marketed by Nippon Shokubei.

The suitable ethoxylated alcohols which enable the formulation of liquid detergent compositions for cool water washing having good suds in the wash are shown to contain 2 to 15 moles of ethylene oxide and have an HLB range between 8 and 18 preferably between 9 and 16 and especially preferred between 10 and 14.

The HLB refers to the hydrophilic – lipophilic balance of the nonionic which is a widely accepted measure of the polarity of a surfactant and its relative affinity for aqueous or hydrocarbon media. The HLB of the nonionic surfactants herein can be experimentally determined in well-known fashion, or can be calculated in the manner set forth in Decker, "Emulsions Theory and Practice" Reinhold (1965), pp. 233 and 248. For example, the HLB of the nonionic surfactants herein can be simply approximated by the term: HLB = E/5 wherein E is the weight percentage of ethylene oxide in the molecule. As indicated by this formula, the HLB will vary, for a given alcohol chain length, with the amount of ethylene oxide present in the molecule.

The highly preferred nonionic surfactants herein include the EO_2–EO_{15} condensates of C_{10} to C_{18} primary and secondary alcohols; the condensates of primary alcohols are most preferred. Non-limiting, specific examples of nonionic surfactants of this type are as follows (the abbreviations used for the nonionic surfactants, e.g., C_{14} $(EO)_6$, are standard for such materials and describe the carbon content of the lipophilic portion of the molecule and the

ethylene oxide content of the hydrophilic portion): n–$C_{14}H_{29}(EO)_5$; n–$C_{14}H_{29}(EO)_6$; n–$C_{14}H_{29}(EO)_7$; n–$C_{14}H_{29}(EO)_{10}$; n–$C_{15}H_{31}$ $(EO)_6$; n–$C_{15}H_{31}$ $(EO)_7$; 2–$C_{15}H_{31}$ $(EO)_7$; n–$C_{15}H_{31}$ $(EO)_8$; 2–$C_{15}H_{31}$ $(EO)_8$; n–$C_{15}H_{31}$ $(EO)_9$; 2–$C_{15}H_{31}$ $(EO)_9$; n–$C_{16}H_{33}$ $(EO)_9$; 2–$C_{16}H_{33}$ $(EO)_9$; and n–$C_{18}H_{35}$ $(EO)_{11}$.

It is to be recognized that mixtures of the foregoing nonionic surfactants are also useful herein and are readily available from commercial alcohol mixtures.

It will be appreciated that the degree of ethoxylation in the nonionics listed herein can vary somewhat, inasmuch as average fractional degrees of ethoxylation occur. For example, n–$C_{15}H_{31}$ $(EO)_7$ can contain small quantities of n–$C_{15}H_{31}$ $(EO)_0$ and n–$C_{15}H_{31}$ $(EO)_{14}$. Commercial mixtures will contain portions of materials of varying EO contents, and the stated EO content represents an average. Such mixtures are quite suitable for use in the present compositions and processes.

Highly preferred alcohol-based nonionic surfactants are the C_{14-15} $(EO)_{6-9}$ materials disclosed hereinabove, which are commercially available as mixtures under the names Neodol 45–7 and Neodol 45–9 from the Shell Chemical Co. Neodol 45–7 is a liquid at ambient temperatures (and is more preferred herein for this reason) whereas Neodol 45–9 is a solid at room temperature. However, solid nonionics such as Neodol 45–9 are also useful in the instant liquid compositions inasmuch as they readily dissolve therein. Other highly preferred nonionics include Dobanol 91–8 ("OXO"-based alcohol from Shell) and Softanol, available from Nippon Shokubei.

When using commercial nonionic mixtures, it is preferred that the un-ethoxylated alcohols and lower $(EO)_1$–$(EO)_2$ ethoxylates be removed, or "stripped", to reduce undesirable odors. Stripping, however, is not a factor in achieving the suds characteristics of this invention.

The Carrier

The third essential component of compositions of this invention is a suitable liquid carrier which is a mixture of water and water-soluble solvents. Such carriers can be used to the extent of from about 20% to about 65%, preferably 40% to 60% by weight of the total composition.

When an alcohol-water mixture is employed as a carrier, the weight ratio of water to alcohol preferably is maintained about 3:1, more preferably from about 4:1 to about 20:1. Higher alcohol (particularly ethanol) concentrations in the water-alcohol mixtures used as carriers herein are preferably avoided because of flammability problems which may arise at such higher alcohol levels, preferably at least 1% water soluble solvent is present.

Any alcohol containing from 1 to about 5 carbon atoms can be employed in the water-alcohol carrier used to prepare the instant detergent compositions. Examples of operable alcohols include methanol, ethanol, propanol, isopropanol, butanol, isobutanol, and pentanol; ethanol is highly preferred for general use.

The Alkanolamine

Desirably, the compositions contain an alkanolamine as a pH buffer. These can be mono-, di-, or tri-ethanolamines; mono-, di-, or tri propanolamines (either normal and/or isopropanolamines); and mono-, di-, or tributanol-amines (normal or iso). Preferably they are used at levels of from about 1% to about 10%, most preferably from 2% to 6%. Mono- and tri-ethanolamines are especially preferred. Most preferred is triethanolamine. Normally higher alkanolamines are mono- or di-substituted. Desirably, the triethanolamine is used to bring the formula to a pH of about 7 to about 7.5 and then monoethanolamine is used to bring the pH to the final position.

Optional Components

Optional, non-essential, non-interfering components can be added to the compositions prepared herein to provide improved performance or aesthetic appeal. For example, compositions containing a color stabilizing agent such as citric acid are preferred from an aesthetic standpoint. Citric acid (or citrate) containing compositions exhibit surprising stability against the tendency of some compositions of the present type to develop a reddening upon storage. In addition, the presence of citric acid in the compositions has a beneficial effect from the standpoint of preventing reddish stains from developing on the outer surfaces of plastic bottles after spillage, seepage or handling of bottles with hands previously contacted with the compositions herein. An amount of citric acid of up to about 1% by weight of composition (based on its free acid form) can be added to obtain these color stabilizing benefits. A highly preferred range for the added citric acid is from about 0.05% to about 0.10% by weight of composition.

Suds modifying agents can be present in the instant compositions in minor proportions to provide high foaming or low foaming products, as desired. While the compositions herein

inherently provide adequate suds levels, some users desire copious lather from laundry detergent products. Accordingly, the compositions herein can optionally contain suds boosters. Anionic surfactants of the ABS-type are quite useful for this suds boosting purpose.

Suds suppressing agents can be present in the instant compositions in minor proportions to provide lower foaming products. While the compositions herein inherently provide adequate suds levels during the wash and good rinsing after the wash, some users desire lower sudsing products for the washing cycle which also improves rinsing. Accordingly, the compositions herein can optionally contain from about 0.5% to about 3% by weight of fatty acids as suds suppressing agents. Useful fatty acids for this purpose consist of those fatty acids containing from about 8 to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms. Suitable fatty acids can be obtained from natural sources such as, for example, plant or animal esters (e.g., palm oil, coconut oil, babassu oil, soybean oil, safflower oil, tall oil, castor oil, tallow, whale and fish oils, lard, grease and mixtures thereof). The fatty acids also can be synthetically prepared (e.g., by the oxidation of petroleum or by hydrogenation of carbon monoxide via the Fischer-Tropsch process). Examples of preferred fatty acids for use as suds suppressing agents are those derived from coconut oil, olive oil and tallow.

Other optional components herein are listed in many commercial publications and include enzymes, bleaching agents, anti-microbial agents, corrosion inhibitors, perfumes and coloring agents. Such components usually will comprise no more than about 1.0% by weight of the total composition.

Preparation and Usage

The compositions herein can be prepared by combining the alkaline earth anionic surfactant with the other indicated components and optional ingredients in a liquid carrier, whereupon the ingredients dissolve to provide a stable, clear liquid composition. The alkaline earth anionic surfactant can be employed in that form, or can conveniently be prepared *in situ* by neutralizing the free acid form of the anionic surfactant with, for example, magnesium hydroxide, etc. Alternatively the alkaline earth metal surfactant can be prepared by simply combining, for example, the sodium salt of the anionic surfactant with, for example, the sodium salt of the anionic surfactant with, for example, a magnesium halide. In such instances a quantity of sodium chloride, or other corresponding electrolyte salt, will be formed which could cause "salting out" effects.

Preferred compositions herein are those which are prepared at a pH in the range from about 7.4 to about 8.4, inasmuch as detergency performance of the surfactant components is increased at pH's at, or above, substantial neutrality. For most purposes, and especially with the magnesium salts, a pH in the range above about 8.5 is preferably avoided, inasmuch as magnesium hydroxide begins to precipitate above that pH. With calcium salts a pH above about 11 is preferably avoided.

While not intending to be limited by theory, it appears that the presence of the alkaline earth metal moiety in the present compositions promotes the efficiency of the anionic surfactant in reducing interfacial tension at interfaces. This reduction in interfacial tension, in turn, promotes detergency. This phenomenon also appears to improve the washing suds characteristics of heretofore unsuitable nonionic surfactants. Accordingly, it is most preferred to use sufficient magnesium ion, calcium ion, or mixtures thereof to provide electrical neutrality to the anionic surfactant and to provide, in addition, from about 3% to about 5% of excess magnesium ion, calcium ion, or mixtures thereof, in the compositions beyond that required for electric neutrality. As noted hereinabove, this quantity of the alkaline earth ion is conveniently and desirably incorporated in the compositions in the form of the metal hydroxides during the *in situ* generation of the alkaline earth metal surfactant via the neutralization process.

Highly preferred compositions prepared in the foregoing manner comprise from about 17% to about 25% by weight (based on the free acid form) of an anionic detersive surfactant selected from the group consisting of the C_9–C_{14} linear alkyl benzene sulfonates, C_9–C_{14} branched-chain alkyl benzene sulfonates, C_9–C_{14} linear alkyl toluene sulfonates, C_9–C_{14} branched-chain alkyl toluene sulfonates, and mixtures thereof; sufficient magnesium ion, calcium ion, or mixtures thereof, especially magnesium ion, to impart electrical neutrality to said anionic surfactant, or mixtures thereof, and to provide, in addition, from about 3% to about 5% by weight of composition of excess magnesium ion, calcium ion, or mixtures thereof; and from about 20% to about 40% by weight of an ethoxylated nonionic detersive surfactant selected from the group consisting of EO_3–EO_{15} ethoxylates of primary and secondary straight-chain and branched-chain alcohols containing from about 8 to about 18 carbon atoms. The balance of the compositions will comprise a liquid carrier selected from the group consisting of water and water-ethanol mixtures. Such compositions will be prepared in the foregoing manner and will be substantially free of agents which cause opacity,

phase separation or brightener precipitation.

The present compositions are used, both as through-the-wash and pre-treatment cleaning agents, in the manner disclosed above. The following examples illustrate the clear stable liquid detergent compositions of the instant invention but are not intended to be limiting thereof.

Laundry Procedure

The procedure consisted of filling the wash tub with water, adding the product, agitating for 1 minute to dissolve the product and then adding a load of naturally soiled clothes. After the clothes were washed they were removed from the wash tub and extracted to remove some of the washing solution. The washing solution in the tub was drained off; the tub rinsed and then filled with water. The extracted clothes were then added back to the wash tub and rinsed with agitation. During the rinse additional water flowed into the tub and the overflow ran into a pipe leading to the drain. Sudsing observations were made during the washing process, during the rinsing operation and when the rinsing time allowed was completed.

Washing machine – top loading semiautomatic; impeller type with reversing agitation; operated manually during the rinse; has built in extractor adjacent to the wash tub.
Model – National NA6050
Manufacturer – MATSUSHITA DENKI SANGYO KK. Washing Machine Division, Osaka, Japan
Agitation – Normal speed, reversing
Wash fill level – 30 liters
Water temperature – 21°C (70°F)
Water hardness – 0.79 grains/liter as $CaCO_3$ (3 gr/U.S. gal.)
Product usage – 30 grams
Fabric load – 1.2 kilograms of naturally soiled clothes
Washing time – 10 minutes
Extraction – 2 minute spin
Rinse – 34 liters of water, as above, 20 minutes rinsing time with normal speed reversing agitation; during rinsing additional water flows into the tub at 10–15 liters/minute and the overflow goes to the drain through an overflow pipe.

The sudsing characteristics of the test products were judged as follows:

During the wash

At the completion of the wash cycle the height of the suds cover was measured in centimeters.

"Typical" suds cover of Japanese granular products on the current retail market is about 3 to 6 cms.

Suds in the rinse

During agitation bubbles of foam are created which collect in the area of the vortex formed by the impeller. The foam cover is estimated according to the scale below every 2 minutes during the rinse and the numbers recorded are averaged to get an overall vortex rinse number. The overall vortex rinse number observed for Japanese granules on the current retail market is in the range of 2 to 4.

(0) Bubbles of water only.
(1) Very slight amount of foam which consists mostly of water-like bubbles.
(2) Very slight amount of foam which consists mostly of detergent type foam.
(3) Slight amount of foam which is detergent foam.
(4) Sufficient detergent foam is formed to cover the vortex.
(5) The detergent foam blankets the vortex area with suds – the approximate volume of suds in the vortex is about 200 cc.
(6) The detergent foam built up has a volume of about 500 cc.

Example I

The following compositions were prepared, examined for stability or gelling and evaluating for suds during the wash and ease of rinsing using the washing procedure outlined above. Compositions 2 and 4 are comparative.

Composition (wt. %)	1	2	3	4
Mg $(C_{11.2av}LAS)_2$	17	–	17	–
Triethanolamine salt of $C_{11.2av}LAS$	–	17	–	17
Tallow Alcohol $(EO)_{11}$	25	25	–	–
$C_{14-15}(EO)_7$	–	–	25	25
Ethyl Alcohol	5	5	5	5
Oleic acid	1	1	1	1
Water & Misc.	← Balance →			
Product form	clear stable liquid	gel with solid separation	clear stable liquid	gel
Washing Suds – cm.	2.0	1.0	–	–
Vortex Rinsing Number	2.1	1.8	–	–

The sudsing results for composition like Composition 2 were as taught in Collins et. al., United States Serial No. 553,331, filed March 4, 1975, which teaches that nonionics having a carbon chain length above 12 exhibit low washing suds in cool water. The easy rinsing observed for Composition 2 was expected in view of the low wash suds. Surprisingly Composition 1, which is within the scope of the instant invention, exhibited observably higher sudsing than Composition 2 during washing and was comparable in rinsing case.

Example II

Additional liquid compositions were formulated and evaluated for washing suds and rinsing ease using the laundry procedure above.

Composition (wt. %)	5	6	7	8	9	10
$MgC_{11.2av}LAS$	17	17	17	17	22.6	17
$C_{9-11}(EO)_8$ stripped	17	17	–	–	19	–
$C_{9-11}(EO)_{12}$ stripped	–	–	21	–	–	–
$C_{14-15}(EO)_3$	–	–	4	–	–	25
Tallow Alcohol $(EO)_{11}$	8	8	–	6	6	–
Softanol 120 ($C_{12-14}(EO)_{12}$)	–	–	–	19	–	–
Ethyl Alcohol	5	5	5	5	5	5
Oleic Acid	–	1	1	1	1	1
Fabric whitening agent	0.3	0.3	0.3	0.3	0.3	0.3
Water & misc.	← Balance →					
Product form	← Clear Liquid →					gel
Washing Suds – cm.	2.8	2.5	4.5	2.2	4.0	0.9
Vortex Rinsing Number	3.3	3.7	4.0	2.8	3.6	1.1

Compositions 5–9 are all within the scope of the invention. The compositions formed were clear stable liquids and in cool water laundering exhibited adequate sudsing during the wash and an ease of rinsing within the range of granular products. Composition 10 is not within the scope of the invention in that the HLB of the nonionic is below 8. It will be noted that the washing suds of Composition 10 was low.

Substantially similar results are observed when the magnesium salt of $C_{11.2}LAS$ in Compositions 5–10 above is replaced by the calcium salt of $C_{11.2}LAS$.

Example III

Additional compositions are formulated and evaluated for washing suds and rinsing ease using the laundry procedure above.

Composition (wt. %)	11	12	13	14	15
Ca salt of Coconut $(EO)_3$ Sulfate	20	–	–	–	–
Mg salt of $C_{11.2av}$ LAS	15	–	–	–	–
Mg salt of Coconut Alkyl Sulfate	–	30	–	20	18
Mg salt of C_{14} α–Olefin Sulfonate	–	–	25	–	–
Tallow Alcohol $(EO)_{11}$	10	10	8	8	5
C_{9-11} Alcohol $(EO)_8$ stripped	15	15	15	–	10
Softanol 120 (C_{12-14} 2^{o}alc. $(EO)_{12}$)	–	–	–	17	–
Ethyl Alcohol	10	5	5	5	–
Water & Misc.	← Balance →				

The above compositions are clear stable liquids which provide adequate washing suds and rinse readily when evaluated by the laundry procedure given above.

Example IV

Composition (wt. %)	16	17	18	19	20	21
Magnesium $C_{11:3}$ alkyl sulfonate	30	30	30	30	30	30
C_{14-15} alkyl poly-ethoxylate (7)	15		–	–		
C_{13-15} secondary alkyl polyethoxylate (7)	–	15	–	–		
C_{12-14} alkyl poly-ethoxylate (6)	–	–	10	–		
C_{12-13} alkyl poly-ethoxylate (3) with E_0 and E_1 essentially removed	–	–	–	10		
Triethanolamine	3	3	–	–	3	3
Monoethanol amine	–	–	4	–	0.5	–
Di isopropanol amine	–	–	–	5		
Oleic acid	2	2	2	–		
Coconut fatty acid	–	–	–	2	1	1
Ethanol	7	7	10	10	6.5	6.5
Brightener and dyes	1.27	1.27	1.5	1.5	1.27	1.27
Water	← Balance →					

WHAT WE CLAIM IS:-

1. A clear stable single phase heavy duty liquid detergent composition, comprising:
(a) from 10% to 50% by weight of the composition based on the free acid form of an anionic detersive surfactant, which is either a sulfate or a sulfonate or mixtures thereof;
(b) sufficient magnesium ion or calcium ion, or mixtures thereof, to neutralize at least 75% of the free acid form of said anionic surfactant;
(c) from 5% to 50% by weight of a nonionic surfactant produced by the condensation of from 2 to 15 moles of ethylene oxide with one mole of a primary or secondary alcohol having a straight or branched alkyl chain containing 8 to 18 carbon atoms, said nonionic surfactant being further characterized by having an HLB of from 8 to 18;
(d) from 0% to 10% of an alkanolamine wherein the alkanol moiety contains from 2 to 4 carbon atoms; and
(e) the balance of the composition comprising mixtures of water and water-soluble solvents, there being at least enough water-soluble solvent to lower the viscosity to 300 centipoise,
said composition having at least 35% by weight of (a) plus (c) and being substantially free of agents which cause phase separation and or gelling.

2. A composition according to claim 1 wherein the total anionic-plus-nonionic surfactant comprises from 35% to 50% by weight of the composition.

3. A composition according to claim 1 or claim 2 wherein the weight ratio of nonionic surfactant to anionic surfactant (free acid form) is in the range from 40:13 to 10:100.

4. A composition according to claim 3 wherein the weight ratio of nonionic surfactant to anionic surfactant (free acid form) is in the range from 25:15 to 10:40.

5. A composition according to Claim 3 wherein the weight ratio of nonionic surfactant to anionic surfactant (free acid form) is in the range from 1:1 to 1:3.

6. A composition according to Claim 3 wherein the weight ratio of nonionic surfactant to anionic surfactant (free acid form) is 1:2.

7. A composition according to any one of claims 1 to 6 wherein the anionic surfactant is selected from alkaryl sulfonates, wherein the alkyl group contains from 9 to 14 carbon atoms, and mixtures thereof; alkyl and olefinic sulfates and sulfonates, wherein the alkyl or olefin group contains from 10 to 18 carbon atoms, and mixtures thereof; ethoxylated alkyl sulfates and sulfonates characterized by an ethylene oxide chain of from 3 to 14 ethoxyl groups and an alkyl group containing from 10 to 18 carbon atoms, and mixtures thereof.

8. A composition according to any one of claims 1 to 7 having a pH in the range from 6 to 8.6.

9. A composition according to any one of claims 1 to 7 having a pH of 7.4 to 8.4.

10. A composition according to Claim 8 or claim 9 comprising an excess of magnesium ion, calcium ion or mixtures thereof, over that needed to provide electrical neutrality of the anionic surfactant.

11. A composition according to claim 10 wherein the excess magnesium ion, calcium ion, or mixtures thereof comprises from 3% to 5% in excess of the amount required to achieve electrical neutrality of the anionic surfactant, said composition being characterized by a pH in the range from 7.4 to 8.4.

12. A composition according to claim 1, comprising:

(a) from 17% to 25% by weight based on the free acid form of an anionic detersive surfactant selected from the group consisting of the C_9–C_{14} linear alkyl benzene sulfonates, branched chain alkyl sulfonates, branched chain alkyl toluene sulfonates, and mixtures thereof;

(b) sufficient magnesium ion, calcium ion, or mixtures thereof, to provide electrical neutrality to said anionic surfactant and to provide, in addition, from 3% to 5% by weight in excess of the amount required to achieve electrical neutrality of the anionic surfactant of magnesium ion, calcium ion, or mixtures thereof;

(c) from 20% to 40% by weight of an ethoxylated nonionic detersive surfactant selected from the group consisting of EO_6–EO_{15} ethoxylates of primary and secondary straight chain and branched chain alcohols containing from 9 to 16 carbon atoms, and mixtures thereof;

(d) the balance of the composition comprising a water-ethanol mixture, there being enough mixture to lower the viscosity to 300 centipoise, said composition having at least 35% by weight of (a) plus (c) and being substantially free of agents which cause phase separation and/or gelling.

13. A clear stable single phase heavy duty liquid laundry composition, consisting essentially of

(a) from 15% to 25% by weight of the composition based on the free acid form of an anionic surfactant which is a linear alkylbenzene sulfonate having an average of 11 to 12 carbon atoms in the alkyl chain;

(b) Sufficient magnesium ion to provide electrical neutrality to the free acid form of said anionic surfactant;

(c) from 20% to 35% by weight of the composition of a nonionic surfactant produced by the condensation of ethylene oxide and a primary or secondary alcohol selected from one mole of tallow alcohol condensed with an average of 11 moles of ethylene oxide, one mole of C_{9-11} primary alcohol condensed with an average of 8 to 12 moles of ethylene oxide, one mole of a C_{14-15} primary alcohol condensed with an average of 6 to 9 moles of ethylene oxide; and mixtures thereof, said nonionic surfactant having an HLB of from 8 to 18;

(d) from 0% to 10% of an alkanolamine wherein the alkanol moiety contains from 2 to 4 carbon atoms; and

(e) the balance of the composition comprising a mixture of water and ethyl alcohol, there being at least enough water-soluble solvent to lower the viscosity to 300 centipoise, said composition having at least 35% by weight of (a) plus (c) and being substantially free of agents which cause phase separation and/or gelling.

14. A composition according to any one of claims 1 to 13 wherein the anionic surfactant is an alkyl benzene sulfonate neutralized with magnesium.

15. A composition according to any one of claims 1 to 13 containing from 15% to 45% by weight of said anionic surfactant and from 10% to 35% of said nonionic surfactant with a ratio of anionic surfactant to nonionic surfactant of from 1:1 to 3:1.

16. A composition according to claim 15 containing from 20% to 40% by weight of said anionic surfactant, and from 10% to 20% by weight of said nonionic surfactant, the ratio of said anionic surfactant to said nonionic surfactant being 2:1.

17. A detergent composition according to claim 1 substantially as described in the Examples.

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